CHEMISTRY LETTERS, pp. 825-826, 1994.

Effect of Substitution of a 2-Anthryl Group at the N=N and N=C Unsaturated Bonds on Their Photoisomerization in the Triplet State

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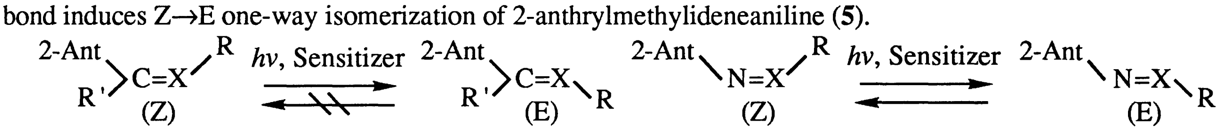
Substitution of a 2-anthryl group at the nitrogen of N=NPh and N=CHPh bonds led to mutual isomerization between Z and E isomers on triplet sensitization giving photostationary mixtures very much rich in E isomers, although the substitution at the carbon of CH=NPh bond resulted in one-way Z→E isomerization in the triplet state likewise to CH=CHPh and $C(CH_3)=NOCH_3$ bonds.

Previously we have shown that substitution of a 2-anthryl group on a carbon of a C=C unsaturated bond solely led to one-way Z→E (cis→trans) isomerization as in 2-styrylanthracene (**1**) in the triplet state[1,2] in contrast to the well-accepted behavior of many olefins like stilbene which undergo mutual isomerization between their Z and E isomers.[3] Subsequently we found that substitution of a 2-anthryl group on the carbon of a C=N unsaturated bond also resulted in one-way Z→E isomerization of N-methoxy-1-(2-anthryl)ethanimine (**2**) in the triplet state.[4] These novel findings as well as the recent active interests in the photochemical behavior of azo compounds[5] for application to optical memory[6] have led us to examine the effect of substitution of a 2-anthryl group at N=N and N=C bonds in their triplet state. We now report that substitution on the nitrogen atoms of the N=NPh and N=CHPh bonds led to mutual isomerization of 2-phenylazoanthracene (**3**) and benzylidene-2-aminoanthracene (**4**) under triplet sensitization; however, a 2-anthryl group on the carbon atom of the CH=NPh bond induces Z→E one-way isomerization of 2-anthrylmethylideneaniline (**5**).



2-Ant: 2-anthryl, X-R: CH-Ph (**1**), $N-OCH_3$ (**2**), N-Ph (**5**)   X-R: N-Ph (**3**), CH-Ph (**4**)
R': H (**1** and **5**), CH_3 (**2**)

In **3**, **4** and **5**, E isomers are generally stable and their direct irradiation produces the corresponding Z isomers (two-way isomerization) which are not very stable at ambient temperature and revert to the E isomers in a thermal process. Therefore, irradiation was carried out at sufficiently low temperature to inhibit thermal reactions to examine their behavior in the triplet state. *E*-**3**, **4** and **5** efficiently quenched the T-T absorption of Eosin Y (triplet energy (E_T): 45 kcal mol^{-1})[7] with rate constants of 3.7, 2.2 and 1.6×10^9 dm^3 mol^{-1} s^{-1}, respectively. For triplet excitation of E-isomers, *E*-**3**, **4** or **5** (1×10^{-5} mol dm^{-3}) were irradiated in the presence of Eosin Y (8×10^{-6} mol dm^{-3}) in EPA (ether:isopentane:ethanol=5:5:2) at 273 K for **3** and 210 K for **4** and **5** with 520 nm light. To examine the behavior of the Z-isomers in the triplet state, *E*-**3**, **4** or **5** were first selectively excited with

330 nm in the presence of Eosin Y to give mixtures of E- and Z-isomers (25, 70 and 45% of Z isomer for **3**, **4** and **5**, respectively), as determined by the absorption spectroscopy,8) which were subsequently irradiated with 520 nm to excite selectively Eosin Y. The resulting isomer ratios were identical with those obtained by triplet sensitized irradiation of the E-isomers with 520 nm. **3** and **4** carrying the 2-anthryl group on the nitrogen atoms of the unsaturated bonds resulted in two-way isomerization by affording photostationary mixtures comprising of 90% E and 10% Z isomers for **3** and 85% E and 15% Z isomers for **4**. On the other hand, **5** gave completely the E isomer on Eosin Y sensitization, thus leading to one-way isomerization likewise to **2**, in contrast to 9-anthrylmethylideneaniline undergoing mutual isomerization on triplet sensitization as well as on direct excitation.9)

On laser (425nm) excitation of benzil (2×10^{-2} mol dm^{-3}; E_T=54 kcal mol^{-1}) as a sensitizer in the presence of *E*-**3**, **4** or **5** (3.3×10^{-4} mol dm^{-3}) in benzene at ambient temperature, the initially resulting benzil triplet state was effectively quenched by them with rate constants of 4.8, 5.1 and 3.6×10^9 dm^3 mol^{-1} s^{-1}, respectively. Then *E*-**4** afforded transient absorptions of the triplet state with λ_{max} at 430, 460, 580 and 640 nm decaying with a less than 200 ns lifetime and *E*-**5** at 430, 460, 570 and 620 nm decaying with a lifetime of 2.0 µs; these absorptions were effectively quenched by oxygen. These absorption spectra are similar to those of the E triplet states of **1** and **2**, which indicates that the observed triplets are assigned to $^3E^*$ and the triplet excitation must be considerably populated in the anthryl moiety likewise to *E*-**1**2) and *E*-**2**. Their shorter lifetimes than those of **1** and **2** may indicate that $^3E^*$ is equilibrated with a less stable triplet state.2) However, the triplet state of *E*-**3** was too short lived to be detected under the present condition. These results indicate that when nitrogen of anil or azo group is conjugated with 2-anthryl moiety, the $^3E^*$ effectively isomerizes competing with its deactivation.

The authors thank the Ministry of Education, Sciences and Culture for their Grant-in-Aid for Specially Promoted Research No. 03101004.

References

1) T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **24**, 2873 (1983); T. Karatsu, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **115**, 9 (1985).
2) T. Arai and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993), and references cited therein; T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi, and K. Tokumaru, *Pure Appl. Chem.*, **60**, 989 (1988).
3) J. Saltiel and Y.-S. Sun, in "Photochromism, Molecules and Systems," ed by H. Duerr and H. Bouas-Laurent, Elsevier, Amsterdam (1990) p. 64, and references cited therein.
4) H. Furuuchi, T. Arai, Y. Kuriyama, H. Sakuragi and K. Tokumaru, *Chem. Lett.*, **1990**, 847; T. Arai, Y. Furuya, H. Furuuchi, and K. Tokumaru, *Chem. Phys. Lett.*, **212**, 597 (1993).
5) H. Rau, in Ref. 3, p. 165 and references cited therein.
6) For example, T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara, and S. Tazuke, *Macromolecules*, **23**, 42 (1990); K. Ichimura, *Yuki Gosei Kagaku Kyokaishi*, **49**, 383 (1991); K. Ichimura, "Photochemical Processes in Organized Molecular Systems," ed by K. Honda, Elsevier, Amsterdam (1991) p. 343.
7) R. W. Chambers and D. R. Kearns, *J. Photochem. Photobiol.*, **10**, 215 (1969).
8) E. Fischer, *J. Phys. Chem.*, **71**, 3704 (1967).
9) H. Görner, E. Fischer and N. Castel, *J. Photochem. Photobiol. A: Chem.*, **52**, 123 (1990).

(Received December 20, 1993)